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ULTRAFAST DYNAMICS AND HIGH RESOLUTION SPECTROSCOPY OF MOLECULES

K. C. Prince

1. **High resolution spectroscopy.**
2. **Time resolved: pump-probe.**
3. **Time-resolved: phase (attosecond) control of double pulses**
4. **Time resolved: interferometric**
5. **Future time-resolved: attosecond pulse trains.**
6. **Source requirements.**

The brief.

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1. ~~A hard and ultrahard X-ray source based on conventional undulator technology and advanced lasing options.~~
2. ~~An ultrahard X-ray source based on in-vacuum undulator.~~
3. ~~A hard and ultrahard X-ray source based on the superconducting undulator technology.~~
4. Soft X-ray FEL line with extended user capabilities.
5. External Seeding using EEHG or cascaded HGHG.
6. ~~THz Coherent radiation generation with spent FEL beam.~~
7. Superradiance for X-ray Production.

Soft x-ray region: carbon, nitrogen, oxygen edges, L edges of 3d metals are available.
Time scales: C, N, O 1s lifetimes – 4-8 fs.

To paraphrase John F. Kennedy (who paraphrased George Bernard Shaw):

Some men see things as they are, and say why;
I dream of spectroscopies that never were (at an XFEL), and say "why not"?

1. **High resolution:** necessary for resonant experiments.

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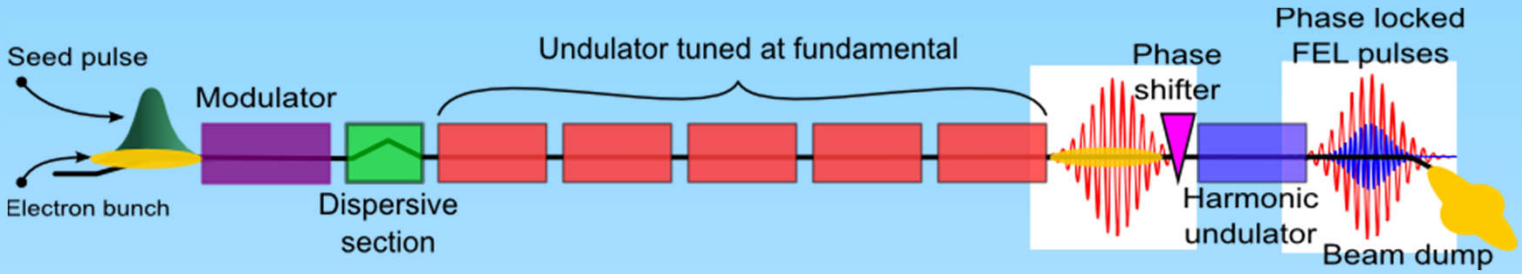
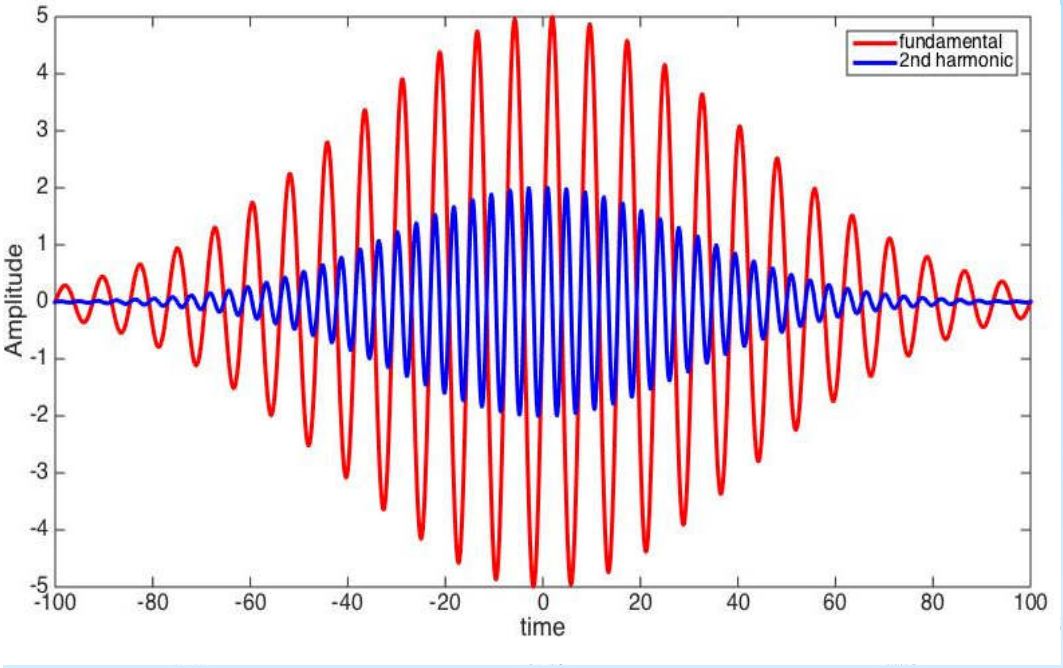
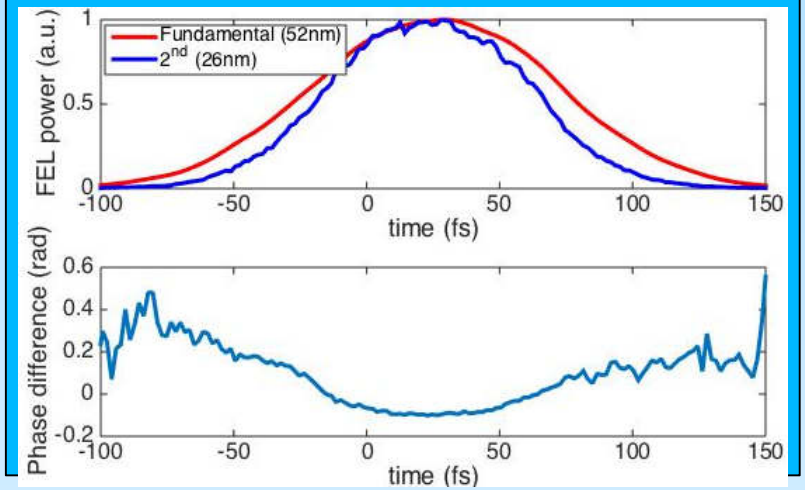


Tuning the **last undulator** to another **harmonic** gives the possibility to **control** the **phase** between **two pulses** with **different commensurate wavelengths**.



GINGER simulations



1. **High resolution:** necessary for resonant experiments.

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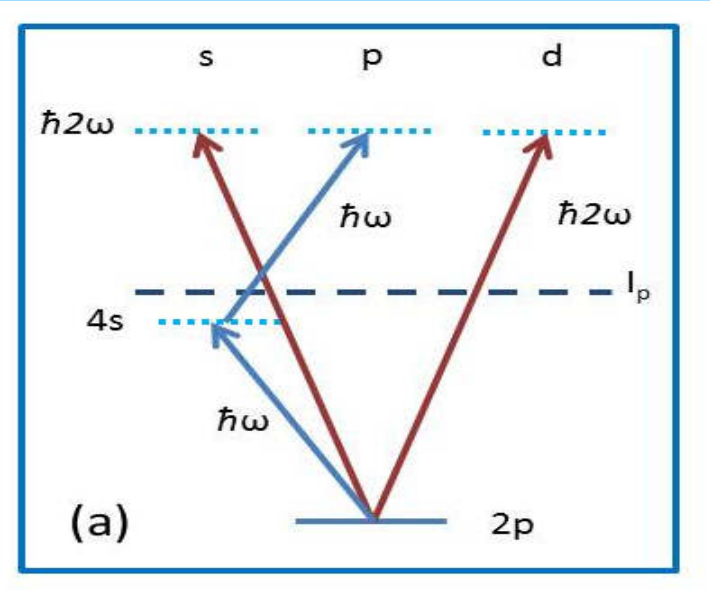
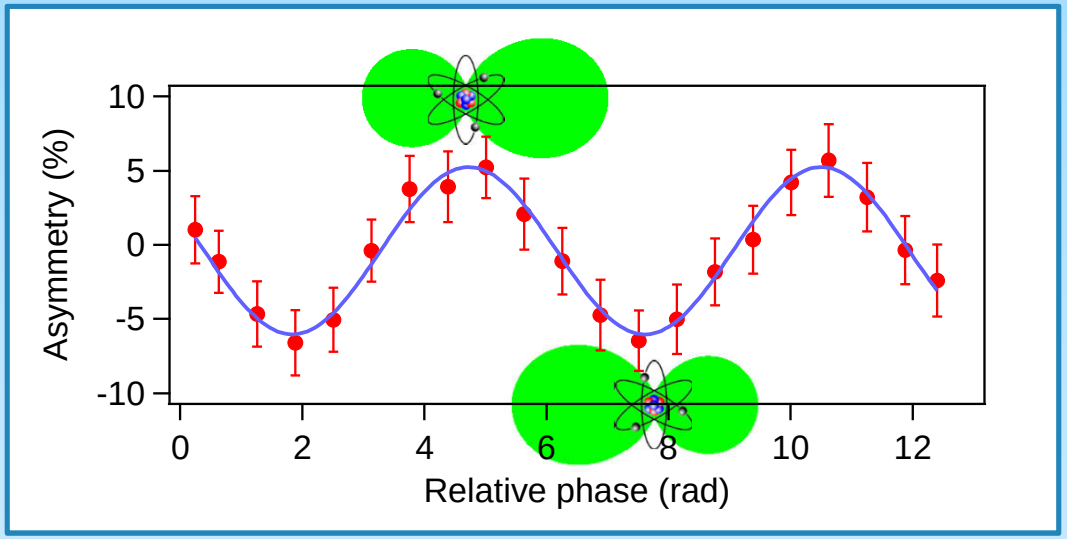
Scheme: two-photon, first harmonic PLUS one-photon, second harmonic ionization of Ne.



$$A_{LR} = \frac{I_L - I_R}{I_L + I_R}$$



$P_1=\cos(\theta)$
$P_2=1/2(3\cos^2(\theta)-1)$
$P_3=1/2(5\cos^3(\theta)-3\cos(\theta))$
$P_4=1/8(35\cos^4(\theta)-30\cos^2(\theta)+3)$

By choosing the Ne $2p^5 4s$ resonance, 62.97 nm, we aim to avoid outgoing *f* waves.

1. **High resolution:** applied to coherent control.

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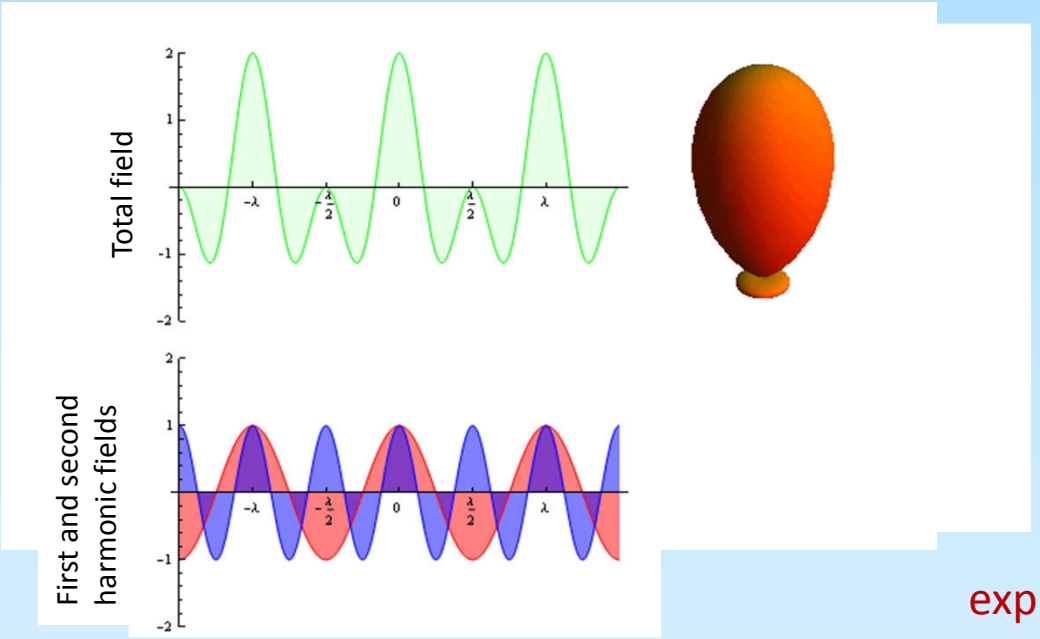
- Left-right asymmetry in photoelectron angular distribution is due to the **interference** between p-wave (**2-photon** process from fundamental) and s/d-wave (**1-photon** process from 2nd harmonic).
- Asymmetry depends on the relative **phase** of **temporally coherent** radiation pulses.



Lobes represent direction and intensity of photo-electron emission from Ne.

exploits 3 attosecond phase resolution, extremely stable, narrow bandwidth.

1. High resolution spectroscopy: two-photon resonances.

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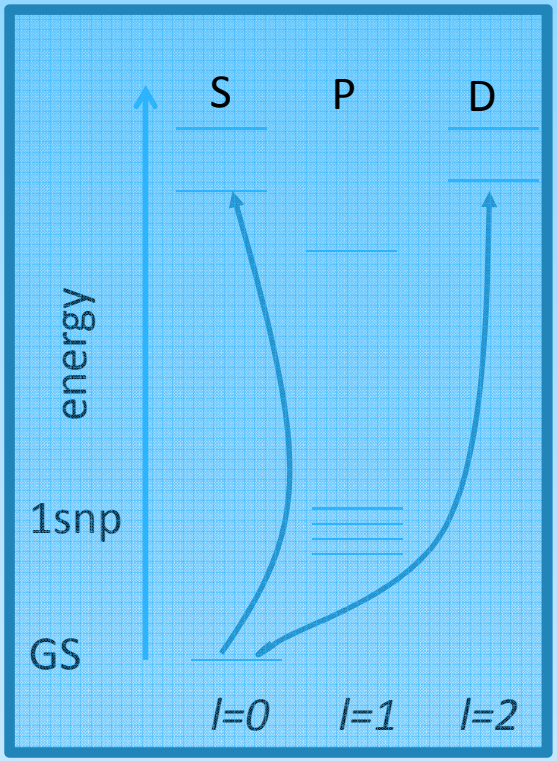
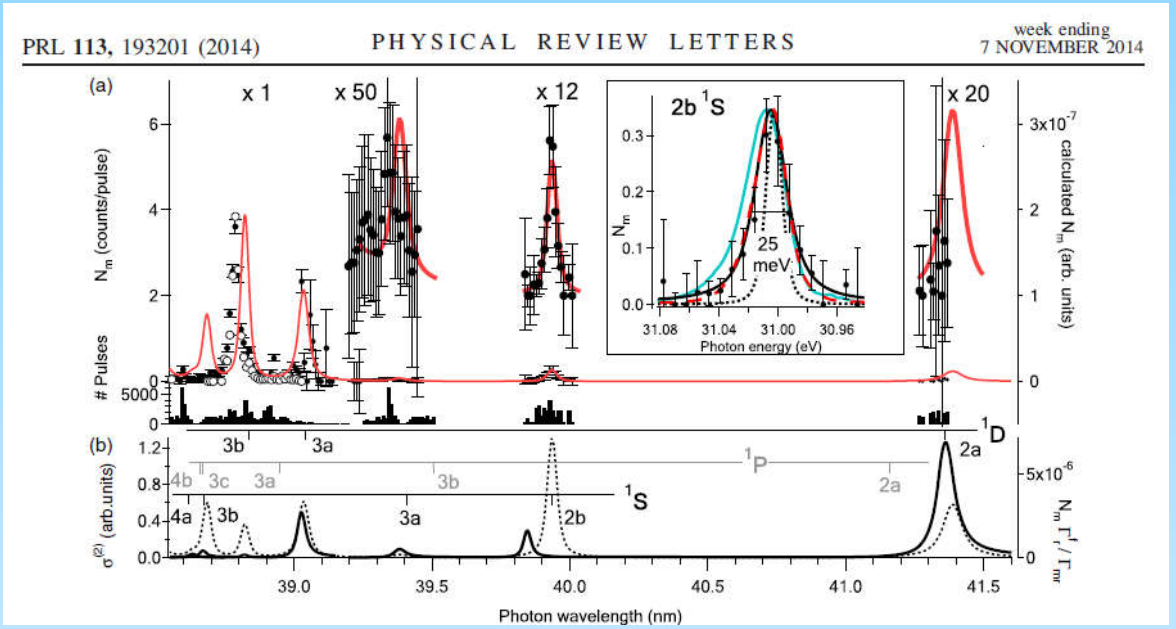


schematic excitations.



Two-photon, doubly excited states of He.
One-particle, two-electron system: the smallest quantum system in which correlation is important.

exploits high intensity, narrow bandwidth

High Resolution Multiphoton Spectroscopy by a Tunable Free-Electron-Laser Light

M. Žitnik,[1,2] A. Mihelič,[1] K. Bučar,[1] M. Kavčič,[1] J.-E. Rubensson,[3] M. Svanquist,[3] J. Söderström,[3] R. Feifel,[3,4] C. Såthe,[5]

1. High resolution spectroscopy: double core holes.

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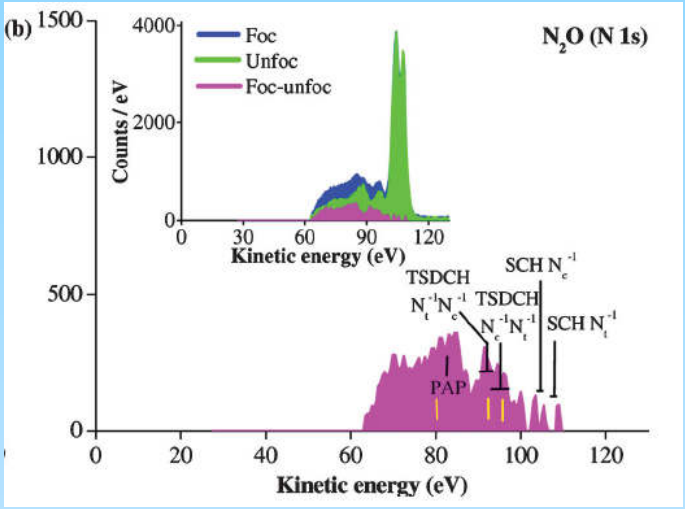
Sequential double core hole spectroscopy:
provides more chemical information
about the target.

Requires higher photon stability (seeded?)
and shorter pulses.



Double-core-hole spectroscopy for chemical analysis with an intense X-ray femtosecond laser

Nora Berrah[a,1], Li Fang[a], Brendan Murphy[a], Timur Osipov[a], Kiyoshi Ueda[b], Edwin Kukk[c], Raimund Feifel[d], Peter van der Meulen[e], Peter Salen[e], Henning T. Schmidt[e], Richard D. Thomas[e], Mats Larsson[e], Robert Richter[f], Kevin C. Prince[f], John D. Bozek[g], Christoph Bostedt[g], Shin-ichi Wada[g,h], Maria N. Piancastelli[d], Motomichi Tashiro[i], and Masahiro Ehara[i]

PNAS **108** (2011) 16912

PRL 111, 073002 (2013) PHYSICAL REVIEW LETTERS week ending 16 AUGUST 2013

Dynamics of Hollow Atom Formation in Intense X-Ray Pulses Probed by Partial Covariance Mapping

L. J. Frasinski,[1,*] V. Zhaunerchyk,[2] M. Mucke,[2] R. J. Squibb,[1,2] M. Siano,[1] J. H. D. Eland,[2,3] P. Linusson,[4] P. v.d. Meulen,[4] P. Salén,[4] R. D. Thomas,[4] M. Larsson,[4] L. Foucar,[5,6] J. Ullrich,[5,7,8] K. Motomura,[9] S. Mondal,[9] K. Ueda,[9] T. Osipov,[10] L. Fang,[10] B. F. Murphy,[10] N. Berrah,[10] C. Bostedt,[11] J. D. Bozek,[11] S. Schorb,[11] M. Messerschmidt,[11] J. M. Glownia,[11] J. P. Cryan,[11] R. N. Coffee,[11] O. Takahashi,[12] S. Wada,[13] M. N. Piancastelli,[2,14] R. Richter,[15] K. C. Prince,[15] and R. Feifel[2,†]

PRL 108, 153003 (2012) PHYSICAL REVIEW LETTERS week ending 13 APRIL 2012

Experimental Verification of the Chemical Sensitivity of Two-Site Double Core-Hole States Formed by an X-Ray Free-Electron Laser

P. Salén,[1,*] P. van der Meulen,[1] H. T. Schmidt,[1] R. D. Thomas,[1] M. Larsson,[1] R. Feifel,[2] M. N. Piancastelli,[2,†] L. Fang,[3] B. Murphy,[3] T. Osipov,[3] N. Berrah,[3] E. Kukk,[4] K. Ueda,[5] J. D. Bozek,[6] C. Bostedt,[6] S. Wada,[6,7] R. Richter,[8] V. Feyer,[8] and K. C. Prince[8,9]

exploits high intensity, short pulse duration.

1. Resonant spectroscopies require **high resolution**.

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Resonant Raman spectroscopy (RIXS)
Coherent Anti-stokes Raman Spectroscopy
Stimulated Raman Adiabatic Passage (STIRAP)
Etc.

Covered yesterday by Nina Rohringer, Thomas Pfeiffer.

REVIEW

doi:10.1038/nature21425

Using coherence to enhance function in chemical and biophysical systems

Gregory D. Scholes[1], Graham R. Fleming[2], Lin X. Chen[3,4], Alán Aspuru-Guzik[5], Andreas Buchleitner[6], David F. Coker[7], Gregory S. Engel[8], Rienk van Grondelle[9], Akihito Ishizaki[10], David M. Jonas[11], Jeff S. Lundeen[12], James K. McCusker[13], Shaul Mukamel[14], Jennifer P. Ogilvie[15], Alexandra Olaya-Castro[16], Mark A. Ratner[17], Frank C. Spano[18], K. Birgitta Whaley[19,20] & Xiaoyang Zhu[21]

IOP PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OP
J. Phys. B: At. Mol. Opt. Phys. **46** (2013) 164008 (12pp) doi:10.1088/0953-4075/46/16/164008

Resonant Auger decay of core-excited CO molecules in intense x-ray laser pulses: the O(1s → π^*) excitation

Ph V Demekhin[1,2,3] and L S Cederbaum[1]

PHYSICAL REVIEW A **84**, 033417 (2011)

Resonant Auger decay of the core-excited C*O molecule in intense x-ray laser fields

Philipp V. Demekhin,* Ying-Chih Chiang, and Lorenz S. Cederbaum

PHYSICAL REVIEW A **94**, 063413 (2016)

Nonlinear resonant Auger spectroscopy in CO using an x-ray pump-control scheme

Song Bin Zhang,[1,2,3,*] Victor Kimberg,[4,5] and Nina Rohringer[2,3,†]

2. Time-resolved = dynamics

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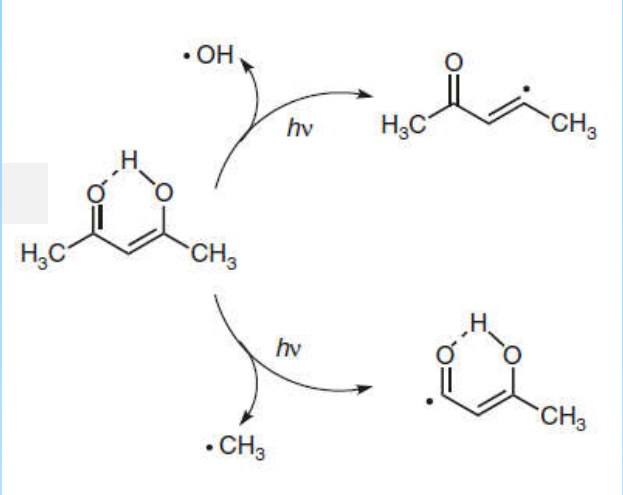
A. Zewail, Nobel Prize for Chemistry, 1999.
Optical lasers.

A recent example from FERMI:
acetylacetone.



On photoexcitation, it dissociates.
The experiment: excite (pump) with UV light, then probe the valence band with FEL light after a given time.

The photoelectron peaks identify the species present.

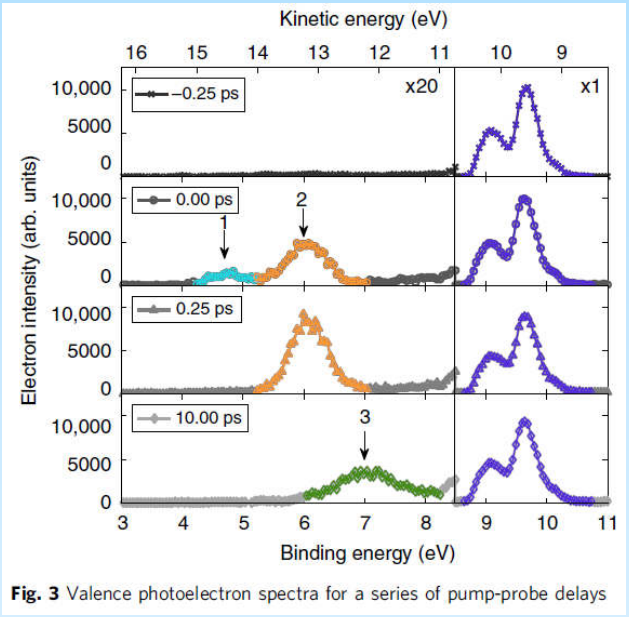


Fig. 3 Valence photoelectron spectra for a series of pump-probe delays

R. Squibb et al, Nature Comm. 9 (2018) 63.
P.I. M. N. Piancastelli,

2. Time-resolved: pump-probe.

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Analysis: the peak areas as a function of time provide populations and lifetimes for various processes. Ions indicate which fragments are formed.

Theory tells us which states are involved and how they evolve.

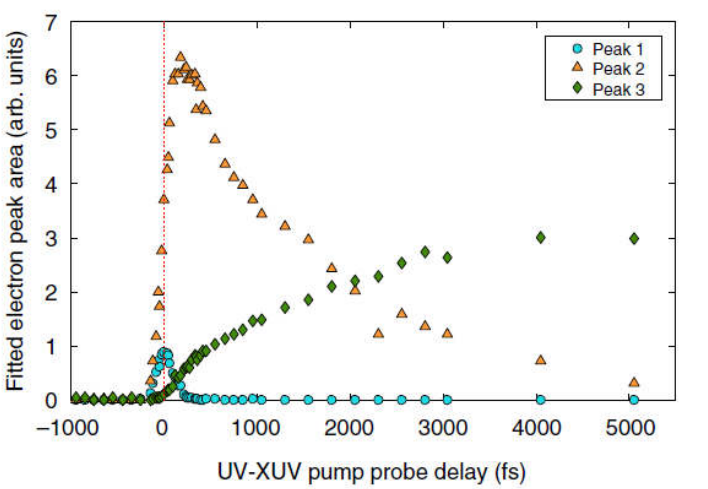

Fig. 4 Experimental peak areas as a function of pump-probe delay. Given for peak 1 (4.64 eV), peak 2 (6.04 eV), and peak 3 (7.14 eV)

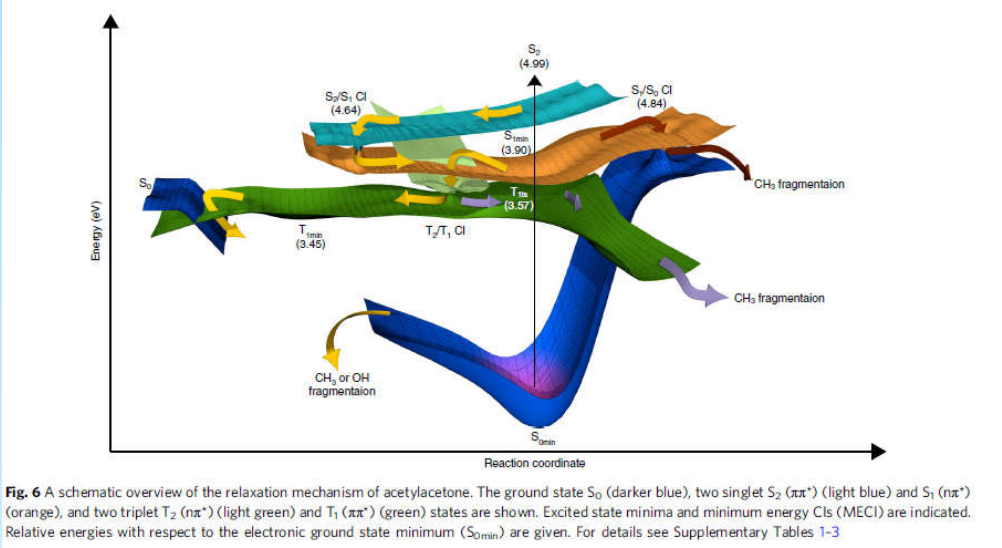

Fig. 6 A schematic overview of the relaxation mechanism of acetylacetone. The ground state S_0 (darker blue), two singlet S_2 ($\pi\pi^*$) (light blue) and S_1 ($n\pi^*$) (orange), and two triplet T_2 ($n\pi^*$) (light green) and T_1 ($\pi\pi^*$) (green) states are shown. Excited state minima and minimum energy CIs (MECI) are indicated. Relative energies with respect to the electronic ground state minimum (S_{0min}) are given. For details see Supplementary Tables 1-3

The excited S_2 state (blue data points) very quickly converts to the lower energy state S_1 (brown points). This then decays more slowly to the T_1 state (green points).

R. Squibb et al, Nature Comm. 9 (2018) 63.
PI: M. N. Piancastelli.

exploits FEL-UV synchronization (7 fs), high intensity.
will work well with core level chemical sensitivity.

3. Time-resolved: phase (attosecond) control of double pulses

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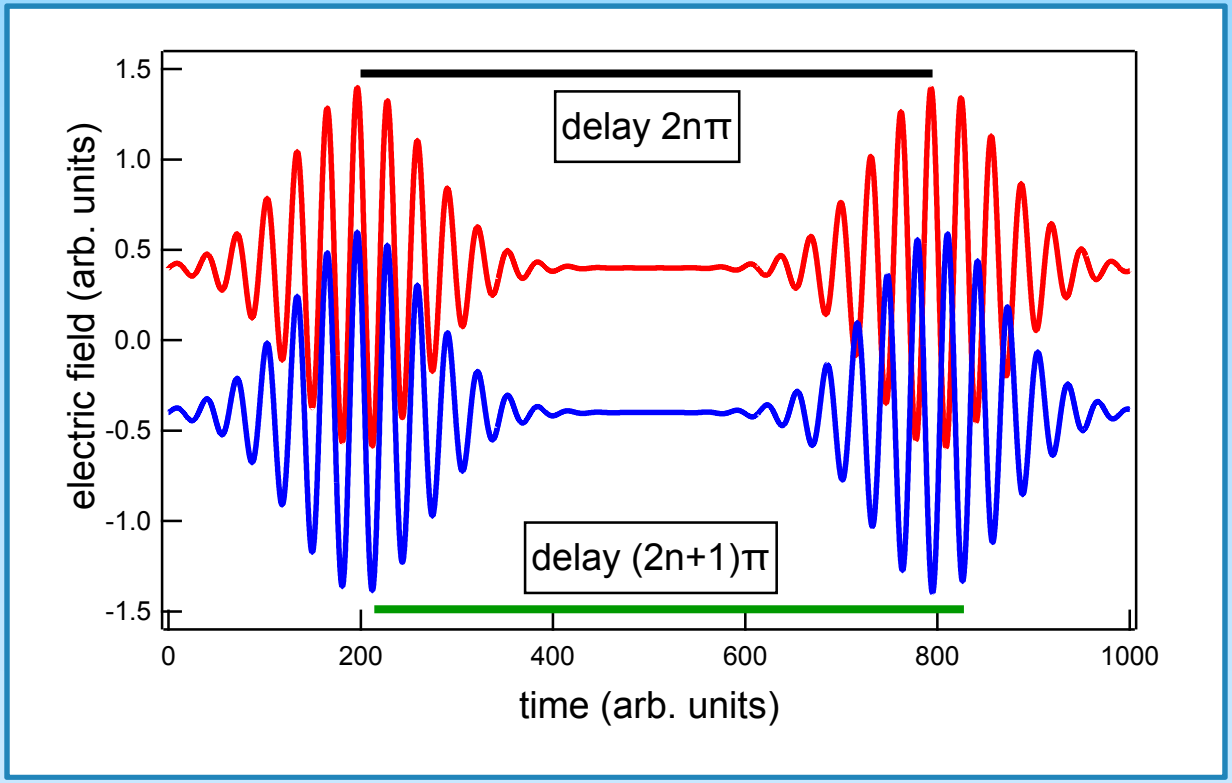

The Tannor-Rice, or pump-dump or pump-control scheme.
The first pulse pumps a target to higher energy. The second pulse:
- if it is in phase, pumps the target from the ground state up to higher energy,
- if it is in antiphase, pumps the target down (dumps) to the ground state.

3. Time-resolved: phase (attosecond) control of double pulses

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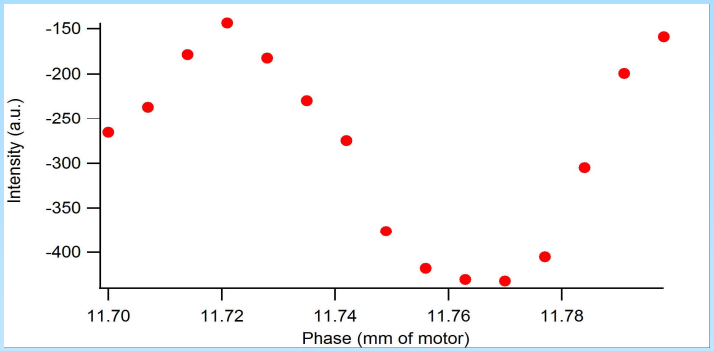
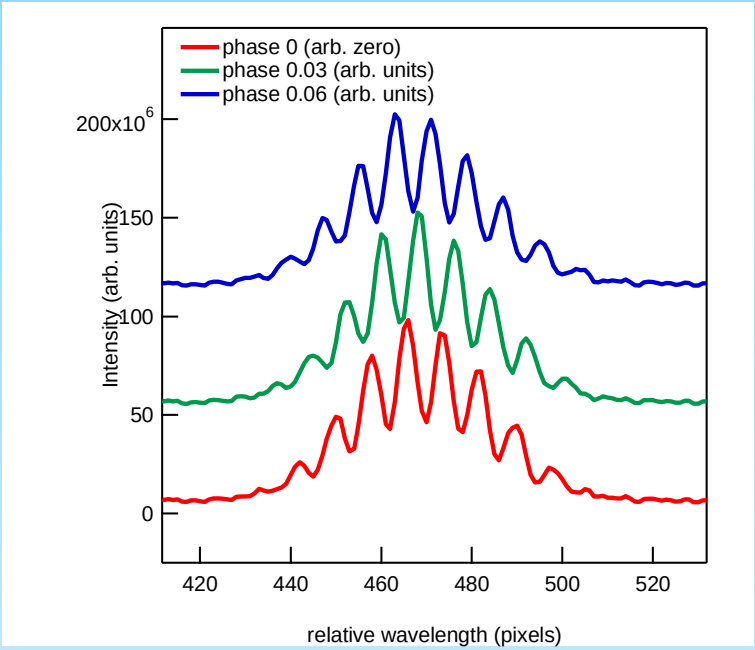
The population (ion signal) oscillates as a function of phase. The second pulse either pumps or dumps, according to phase. Period: 170 attoseconds.

He Rydberg state population



pulses in phase

pulses out of phase



Optical interference patterns as a function of phase.

Also known as Ramsey fringes.

exploits extremely accurate – few attoseconds – temporal resolution.
Double seeding required.

4. Time-resolved: interferometric.

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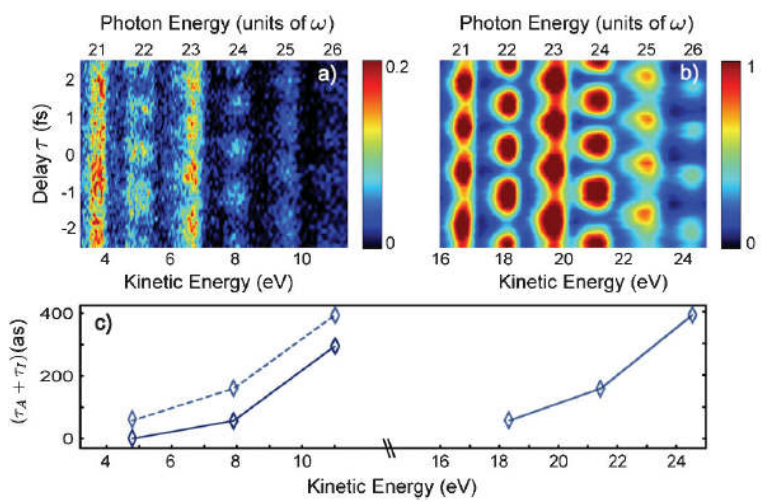

FIG. 2 (color). Energy spectra as a function of delay from electrons liberated from the 3*s* shell (a) and the 3*p* shell (b), respectively. (c) Retrieved delays corrected for the Cr group delay. Also shown are the 3*p* delays shifted down in energy for comparison with the 3*s* delays (dashed line).

An interferometric technique, using pulse trains: RABBITT

Reconstruction of Attosecond Beating By Interference of Two-photon Transitions.

Ionization of Ar 3s and 3p by an attosecond pulse train, in the presence of an IR pulse.

K. Klunder et al, Phys. Rev. Lett. 106 (2011) 143002

RABBITT uses an IR pulse as a kind of reference.
Corrections are necessary for the effect of the IR field.
Can we do without it?

4. Time-resolved: interferometric.

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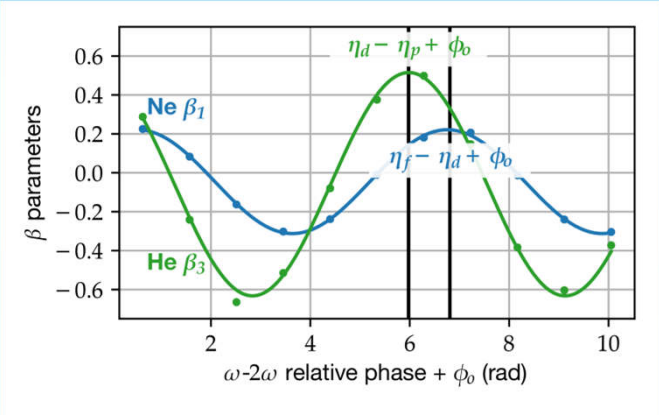

Use first and second harmonics, and scan phase.
Observe the changes in odd β parameters.
β parameters <-> angular momentum
<-> partial waves.

Extract Wigner time delay – experimental resolution 3 attoseconds.

See talk of Kiyoshi Ueda.

5. Future time-resolved: attosecond pulse trains.

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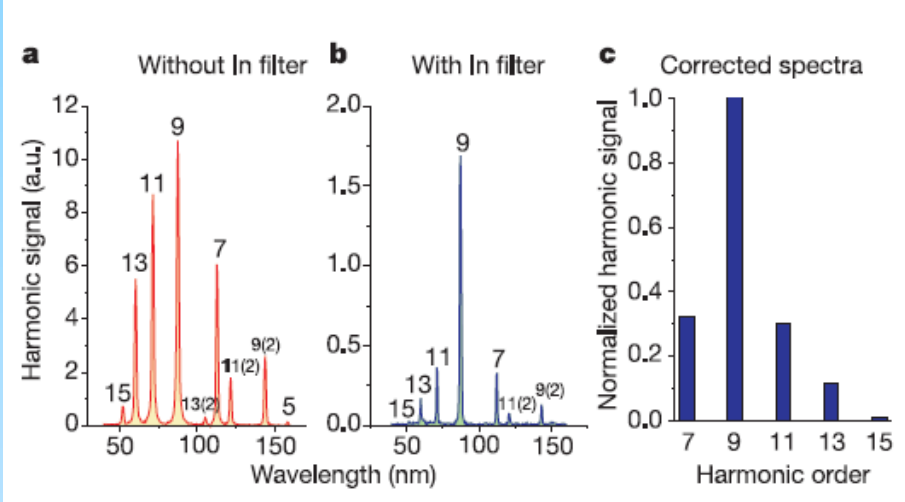
Pulse sculpting or tailoring?
e.g. Tzallas et al measured a train of pulses with width 780 as.

Can we extend this to molecules?
And to solids?
How short can the wavelength be?



Tzallas et al, Nature 426 (2003) 427.

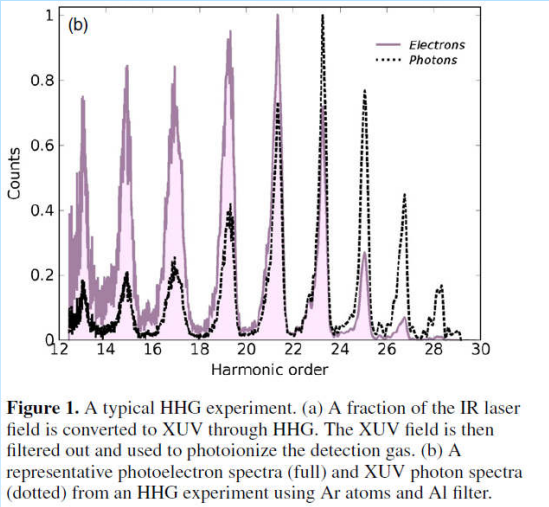
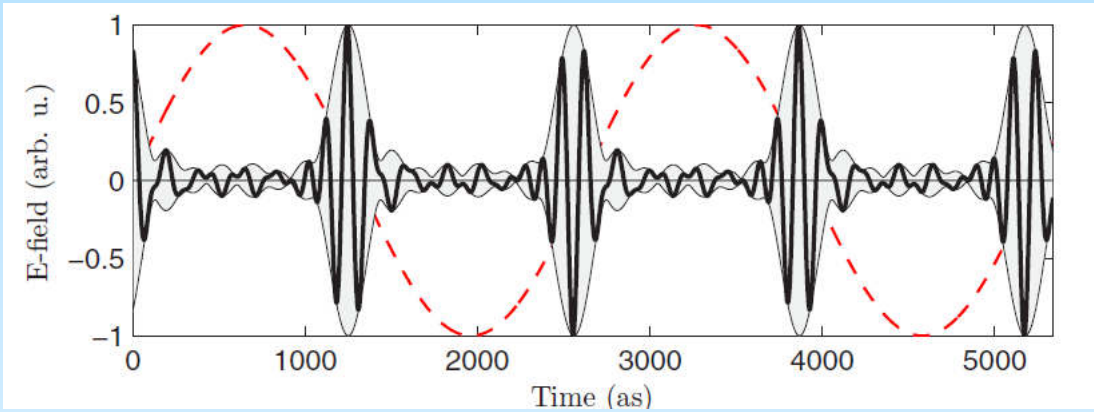


Figure 1. A typical HHG experiment. (a) A fraction of the IR laser field is converted to XUV through HHG. The XUV field is then filtered out and used to photoionize the detection gas. (b) A representative photoelectron spectra (full) and XUV photon spectra (dotted) from an HHG experiment using Ar atoms and Al filter.



Frequency domain

Time domain.

J. M. Dahlstrom et al, J. Phys. B: At. Mol. Opt. Phys. 45 (2012) 183001

6. Time-resolved: attosecond pulse trains.

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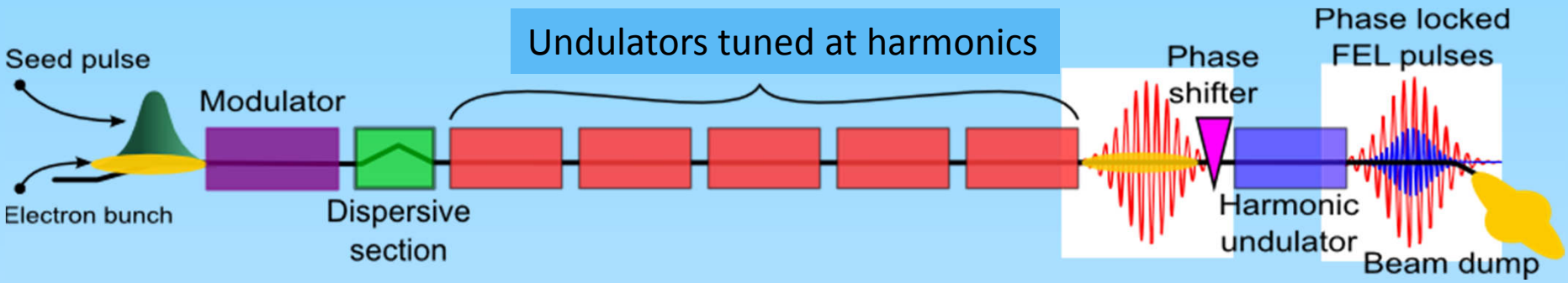

By tuning each undulator at a successive harmonic, and setting the phase correctly, a train of attosecond pulses can be generated. First experiments have been completed.

Chirality

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ARTICLES
https://doi.org/10.1038/s41567-017-0038-z
nature physics

Photoexcitation circular dichroism in chiral molecules

S. Beaulieu[1,2], A. Comby[1], D. Descamps[1], B. Fabre[1], G. A. Garcia[3], R. Géneaux[4], A. G. Harvey[5], F. Légaré[2], Z. Mašín[5], L. Nahon[3], A. F. Ordonez[5,6], S. Petit[1], B. Pons[1*], Y. Mairesse[1*], O. Smirnova[5,6*] and V. Blanchet[1]

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
ACS AuthorChoice
Letter
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Relaxation Dynamics in Photoexcited Chiral Molecules Studied by ...: Toward Chiral

... Descamps,[†] Francois Légaré,[‡] ...iresse,[†] and Valérie Blanchet[*,†]

Attosecond-resolved photoionization of chiral molecules

S. Beaulieu,[1,2*] A. Comby,[1] A. Clergerie,[1] J. Caillat,[3] D. Descamps,[1] N. Dudovich,[4] B. Fabre,[1] R. Géneaux,[5] F. Légaré,[2] S. Petit,[1] B. Pons,[1] G. Porat,[4] T. Ruchon,[5] R. Taïeb,[3] V. Blanchet,[1] Y. Mairesse[1]

Flexible design.

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The FERMI machine physics team has developed modes of operation that were not considered (or considered impossible) before construction.

- Phase control of two overlapping hamonics.
- Phase control of temporally separated pulse. Gauthier et al, PRL 115, 114801 (2015). PRL 116, 024801 (2016).
- Exploitation of chirp. De Ninno et al, PRL 110 , 064801 (2013).
- XUV pump-probe pulses at very different wavelengths, with control of the delay. E. Ferrari et al., Nat. Commun. 7, 10343 (2016).
- Overlapping, incommensurate, phase locked wavelengths. Roussel et al, PRL 115, 214801 (2015).
- Spectrotemporal pulse shaping. Gauthier et al, PRL 115, 114801 (2015).

EEHG at FERMI

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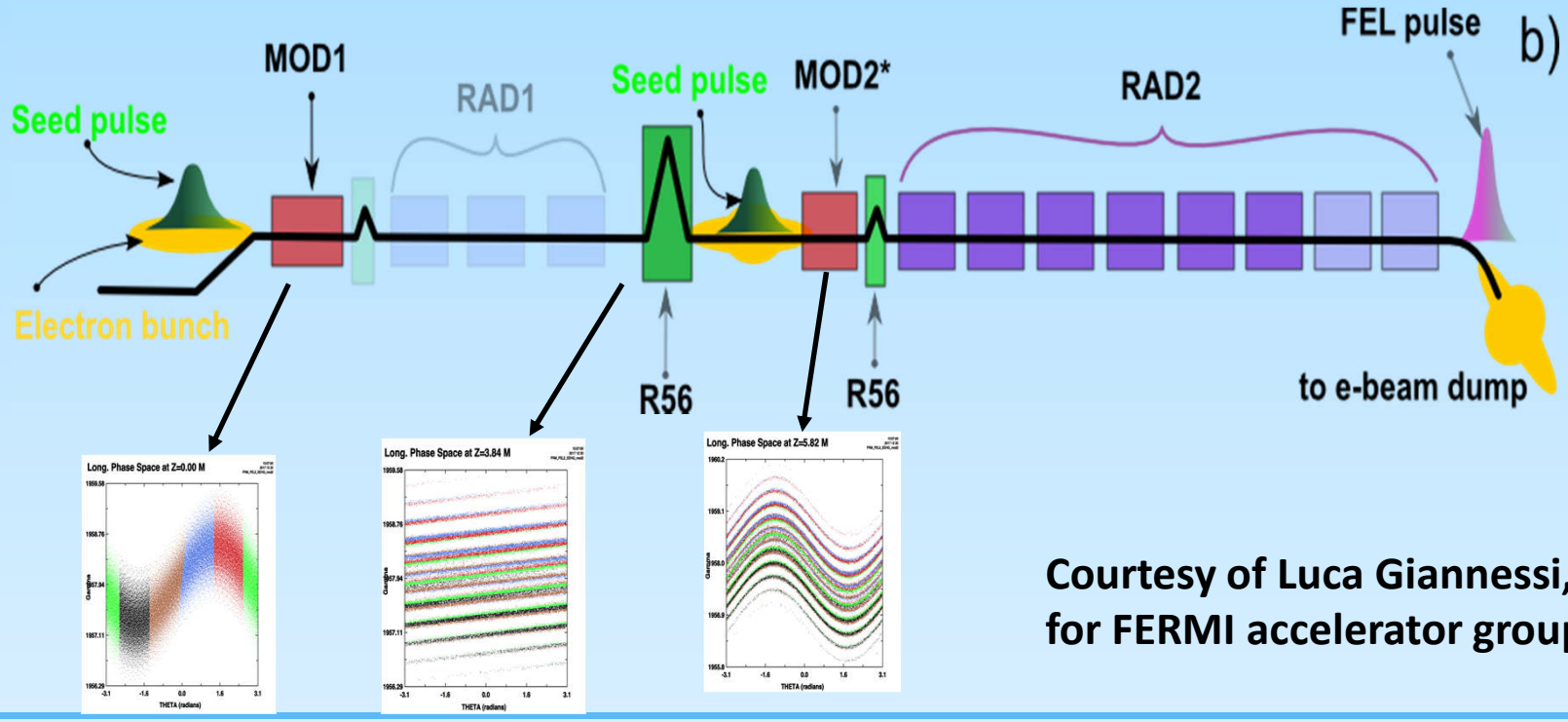
In May-August 2018 the FERMI FEL-2 was modified to test EEHG modulation and amplification in the VUV-Soft X-ray spectral range.
The layout was modified as follows :

1. First radiator (RAD1) open and not used.
2. Second modulator (MOD 2) replaced with a long period module to ensure resonance with a seed at 260 nm
3. Delay line used as the first strong dispersion.
4. Second laser injection before MOD 2



Courtesy of Luca Giannessi, for FERMI accelerator group.

EEHG spectra at soft x-ray wavelengths.

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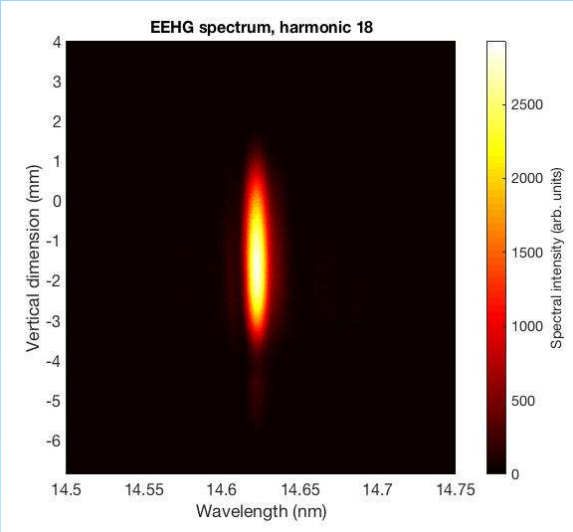
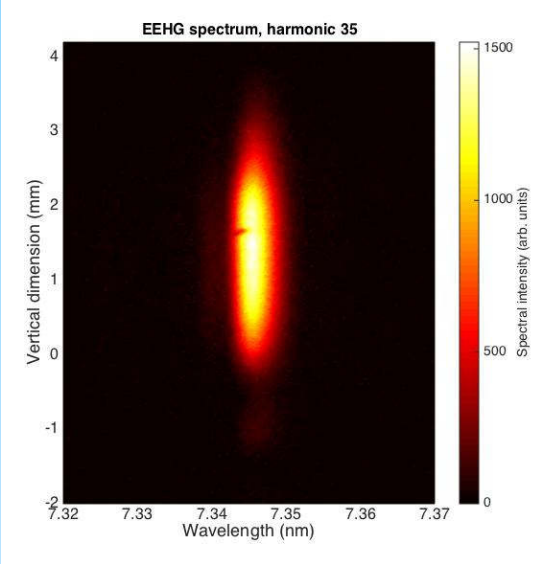
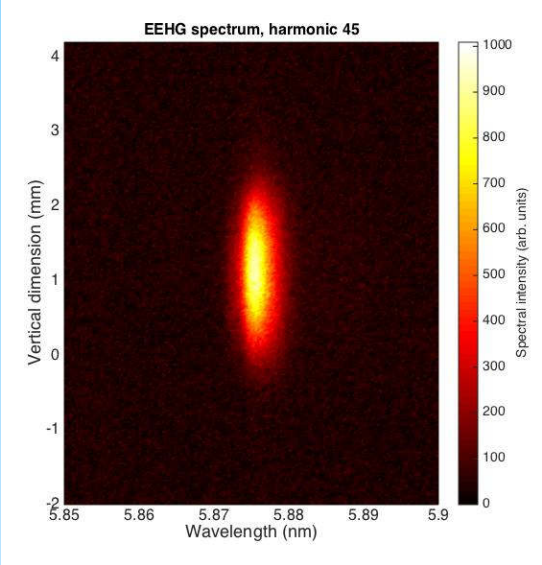
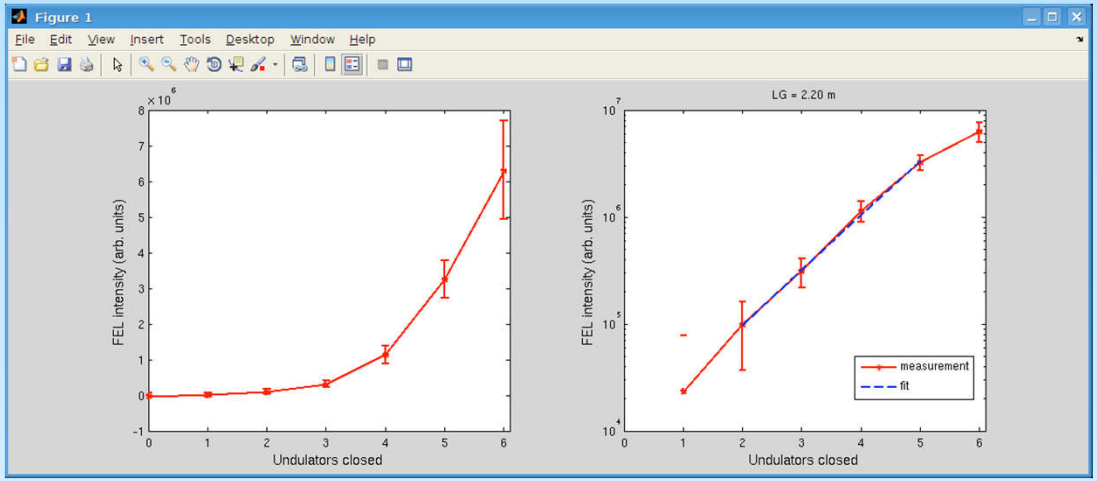






With recent experiments at FERMI we have measured FEL pulses with ~10 µJ down to 6 nm with very narrow bandwidth spectra.

Clear indication of FEL amplification is demonstrated with exponential growth of the power along the radiator.



Courtesy of Luca Giannessi, for FERMI accelerator group.

7. Which source for this science?

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High spectral and temporal resolution
-> control quantum systems
-> photochemistry
-> dynamics.

Short pulses, < 10 fs, preferably less.
Multi colour for coherent control, Raman class, etc experiments.
Phase control for double pulses.
Full polarization control (**chiral dynamics?**)
(Near) transform limited.
UV-FEL jitter < 1 fs – unless you use interferometry.
Flexible design.

Seeded? EEHG? Superradiance?

User communities: FELs are a "marriage of inconvenience" between lasers and synchrotrons – they combine the disadvantages of both (and the advantages.)

To engage with laser scientists – a possible strategy is to use the techniques they know.

4. Soft X-ray FEL line with extended user capabilities

- Extended tunability range.
- Lower photon energies.
- Pump-probe experiments, independent FEL colors.
- Full polarization control.
- Significant increase of the coherence time.

5. External Seeding using EEHG or cascaded HGHG

- Wavelength could be down to 2 nm
- Repetition rate up to 100 kHz.
- Pulse duration around 6 fs (300 microJ)
- 0.08% bandwidth.
- EEHG simulations - similar parameters at 230 eV (5.4 nm).

7. Superradiance for X-ray Production

- High power, very short pulses comparable to the coherence time.
- Peak power an order of magnitude higher than normal.

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Elettra Sincrotrone Trieste

Two colour.

nature photonics

LETTERS

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Coherent control with a short-wavelength free-electron laser

K. C. Prince[1,2,3]*, E. Allaria[1], C. Callegari[1], R. Cucini[1], G. De Ninno[1,4], S. Di Mitri[1], B. Diviacco[1], E. Ferrari[1], P. Finetti[1], D. Gauthier[1], L. Giannessi[1,5], N. Mahne[1], G. Penco[1], O. Plekan[1], L. Raimondi[1], P. Rebernik[1], E. Roussel[1], C. Svetina[1,6], M. Trovò[1], M. Zangrando[1,3], M. Negro[7], P. Carpeggiani[7], M. Reduzzi[7], G. Sansone[7]*, A. N. Grum-Grzhimailo[8], E. V. Gryzlova[8], S. I. Strakhova[8], K. Bartschat[9], N. Douguet[9], J. Venzke[9], D. Iablonskyi[10], Y. Kumagai[10], T. Takanashi[10], K. Ueda[10]*, A. Fischer[11], M. Coreno[12], F. Stienkemeier[13], Y. Ovcharenko[14], T. Mazza[15] and M. Meyer[15]

Two photon resonant excitation.

PRL 113, 193201 (2014) PHYSICAL REVIEW LETTERS week ending 7 NOVEMBER 2014

High Resolution Multiphoton Spectroscopy by a Tunable Free-Electron-Laser Light

M. Žitnik,[1,2] A. Mihelič,[1] K. Bučar,[1] M. Kavčič,[1] J.-E. Rubensson,[3] M. Svanquist,[3] J. Söderström,[3] R. Feifel,[3,4] C. Såthe,[5] Y. Ovcharenko,[6] V. Lyamayev,[7] T. Mazza,[8] M. Meyer,[8] M. Simon,[9,10] L. Journel,[9,10] J. Lüning,[9,10] O. Plekan,[11] M. Coreno,[11] M. Devetta,[11] M. Di Fraia,[12] P. Finetti,[11] R. Richter,[11] C. Grazioli,[11] K. C. Prince,[11,13] and C. Callegari[11]

Pump-probe.

Acetylacetone photodynamics at a seeded free-electron laser

R.J. Squibb[1], M. Sapunar[2], A. Ponzi[2], R. Richter[3], A. Kivimäki[4], O. Plekan[3], P. Finetti[3], N. Sisourat[5], V. Zhaunerchyk[1], T. Marchenko[5], L. Journel[5], R. Guillemin[5], R. Cucini[3], M. Coreno[3,6], C. Grazioli[3,6], M. Di Fraia[3,6], C. Callegari[3,6], K.C. Prince[3,7], P. Decleva[4,8], M. Simon[5], J.H.D. Eland[1,9], N. Došlić[2], R. Feifel[1] & M.N. Piancastelli[5,10]

Double core hole.

PRL 108, 153003 (2012) PHYSICAL REVIEW LETTERS week ending 13 APRIL 2012

Experimental Verification of the Chemical Sensitivity of Two-Site Double Core-Hole States Formed by an X-Ray Free-Electron Laser

P. Salén,[1,*] P. van der Meulen,[1] H. T. Schmidt,[1] R. D. Thomas,[1] M. Larsson,[1] R. Feifel,[2] M. N. Piancastelli,[2,†] L. Fang,[3] B. Murphy,[3] T. Osipov,[3] N. Berrah,[3] E. Kukk,[4] K. Ueda,[5] J. D. Bozek,[6] C. Bostedt,[6] S. Wada,[6,7] R. Richter,[8] V. Feyer,[8] and K. C. Prince[8,9]

Thank you for your attention.